

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 81301562.5

(51) Int. Cl.³: **C 10 M 1/14**
C 10 M 3/08

(22) Date of filing: 09.04.81

(30) Priority: 08.05.80 US 147707

(43) Date of publication of application:
18.11.81 Bulletin 81/46

(84) Designated Contracting States:
BE DE FR GB IT NL

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(54) Lubricating oil composition containing sediment-reducing additive.

(57) Lubricating oil compositions which contain polycarboxylic acid-glycol esters as friction modifiers in combination with hydrocarbon soluble alkenyl succinimide dispersants with reduced tendency toward formation of sediment upon storage through addition of small proportions of polyol or polyol anhydride partial ester of a fatty acid or an ethoxylated fatty acid, amine or amide stabilizer. Glycerol oleates are preferred stabilizer additive.

EP 0 039 998 A1

1 LUBRICATING OIL COMPOSITION CONTAINING
2 SEDIMENT-REDUCING ADDITIVE

3 This invention relates to storage stable lubri-
4 cating oil compositions containing an additive package
5 which provides both dispersant and friction modification
6 properties. More particularly, this invention relates
7 to a formulated lubricating oil composition containing a
8 polycarboxylic acid-glycol ester friction modifier and
9 an alkenyl succinimide dispersant having a reduced ten-
10 dency to form sediment upon storage.

11 Lubricating oil compositions which contain
12 polycarboxylic acid-glycol esters as friction reducing
13 components are known in the art and are disclosed, for ex-
14 ample, in U.S. Patent 4,105,571 issued August 8, 1978 to
15 Shaub et al. The oil-soluble alkenyl succinimide disper-
16 sants, particularly polyisobutenyl succinimide disper-
17 sants, are well-known and are disclosed in U.S. Patent,
18 3,172,892, issued March 9, 1965 to Le Suer et al., and
19 U.S. Patent 3,933,659, issued January 20, 1976 to Lyle
20 et al.

21 It is known that lubricating oil compositions
22 containing the aforesaid alkenyl succinimide dispersants
23 and polycarboxylic acid-glycol ester friction modifiers
24 offer a number of advantageous properties, however, a
25 problem frequently encountered is the tendency of appre-
26 ciable quantities of sediment to form upon storage of
27 formulated compositions containing these additives and
28 other conventionally employed additives, especially metal
29 containing additives. The present invention deals with
30 this problem by providing additives found effective in
31 stabilizing such compositions against sediment formation,
32 the stabilizer additives being certain polyol-fatty acid
33 esters or ethoxylated fatty acids, amines or amides.

34 Shaub et al in U.S. Patent 4,105,571 disclose
35 that incompatibility problems of zinc dihydrocarbyl di-
36 thiophosphate and glycol ester friction-reducing compon-
37 ents can be resolved by pre-dispersing either component
38 in an ashless dispersant prior to combining them in the

1 lubricating oil formulation; however, Shaub et al do note
2 that formulations containing dispersants based on a re-
3 action product of polyisobutenyl succinic anhydride and
4 polyamine exhibited evidence of storage instability and
5 suggested that an increased amount of dispersant may be
6 necessary to maintain compatibility. The present inven-
7 tion deals with this problem by providing a stabilizer
8 additive found effective in compatibilizing the composi-
9 tions disclosed herein or enhancing the compatibility of
10 said components.

11 In accordance with the present invention, there
12 are provided storage stable lubricating oil compositions
13 having a reduced tendency to form sediment comprising:

- 14 (a) a polycarboxylic acid-glycol ester fric-
15 tion reducing component,
- 16 (b) an oil-soluble alkenyl succinimide or bor-
17 ated alkenyl succinimide dispersant, and
- 18 (c) an oil-soluble stabilizer additive being
19 a polyol or polyol anhydride partial ester
20 of a C₈-C₂₂ fatty acid or an ethoxylated
21 fatty acid, fatty amine or fatty amide, in
22 an amount effective to reduce the tendency
23 of said lubricating oil formulation to
24 form sediment.

25 The term lubricating oil composition as used
26 herein is meant to refer to fully formulated compositions
27 intended for use, for example as crankcase motor oils
28 which contain a number of conventionally used additives
29 in the usual amounts especially oxidation inhibitors,
30 rust inhibitors, viscosity index improvers, such as ole-
31 fin copolymers, pour depressants, oil-soluble detergent
32 additives such as the neutral and basic metal phenates,
33 sulfurized phenates and sulfonates, such as the calcium
34 and magnesium sulfurized phenates and sulfonates, as well
35 as the zinc dialkyl dithiophosphates which are useful anti-oxidant
36 and anti-wear additives. It is believed that the metal con-

1 taining additives such as the normal and basic metal sul-
2 fonates, phenates and sulfurized phenates and metal di-
3 thiophosphates contribute to the tendency of lubricating
4 oil compositions to form sediment when in the presence
5 of the ester friction reducing components and alkenyl suc-
6 cinimide dispersant. The metal phenates and sulfonates
7 noted above are typically employed in amounts of from
8 about 2 to 5 weight percent and metal dithiophosphates
9 are usually found in fully formulated lubricating oil com-
10 positions in amounts from about 1 to 3 weight percent.

11 The friction reducing esters are generally de-
12 rived from the esterification of a polycarboxylic acid
13 with a glycol and may be partial esters or diesters of
14 the formulas:

15
$$\text{HO-R}'\text{-OOC-R-COOH and HO-R}'\text{-OOC-R-COOR}''\text{-OH}$$

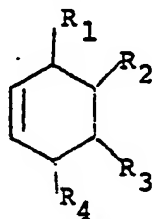
16 wherein R is the hydrocarbon radical of the acid and R'
17 and R'' is either the hydrocarbon radical of an alkane
18 diol or the oxy-alkylene radical from an oxa-alkane diol
19 as defined hereinbelow. The polycarboxylic acid may be
20 an aliphatic saturated or unsaturated acid and will gen-
21 erally have a total of about 24 to 90, preferably about
22 24 to 60, carbon atoms and about 2 to 3, preferably about
23 2, carboxylic acid groups with at least about 9 carbon
24 atoms, preferably about 12 to 42, especially 16 to 22 car-
25 bon atoms between the carboxylic acid groups. Generally
26 about 1-3 moles of glycol, preferably 1-2 moles of glycol,
27 are used per mole of acid to provide either a complete or
28 partial ester.

29 Also, esters can be obtained by esterifying a
30 dicarboxylic acid or mixture of such acids with a diol
31 or mixture of diols, in which case R would then be the
32 hydrocarbon radical of the dicarboxylic acid and R' and
33 R'' would be the hydrocarbon radicals associated with the
34 diol or diols.

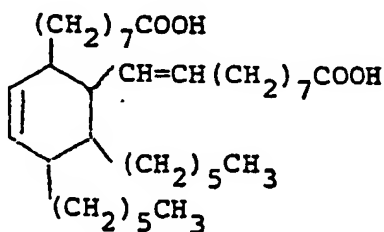
35 The friction reducing esters are typically used
36 in amounts ranging from about 0.01 percent to 2 percent

1 by weight, more preferably 0.05 to 0.5 percent by weight
 2 based upon the overall weight of the lubricating oil com-
 3 position, more preferably, formulations containing 0.1
 4 to 0.3 weight percent are highly effective.

5 Especially preferred are the dimer acid ester
 6 friction reducing esters. The term dimer acid used here-
 7 in is meant to refer to those substituted cyclohexene di-
 8 carboxylic acids formed by a Diels-Alder-type reaction
 9 which is a thermal condensation of C_{18} - C_{22} unsaturated
 10 fatty acids, such as tall oil fatty acids, which typical-
 11 ly contain about 85 to 90 percent oleic or linoleic acids.
 12 Such dimer acids typically contain about 36 carbon atoms.
 13 The dimer acid structure can be generalized as follows:



20 with two of the R groups being carboxyl groups and two be-
 21 ing hydrocarbon groups depending upon how the condensation
 22 of the carboxylic acid has occurred. The carboxyl groups
 23 can be $-(CH_2)_8COOH$; $-CH=CH(CH_2)_8COOH$; $-(CH_2)_7COOH$;
 24 $-CH_2-CH=CH(CH_2)_7COOH$; $-CH=CH(CH_2)_7COOH$ and the hydrocarbon
 25 terminating group can be represented by: $CH_3(CH_2)_4-$;
 26 $(CH_3(CH_2)_5-$; $CH_3(CH_2)_7-$; $CH_3(CH_2)_4CH=CH-$; $CH_3(CH_2)_4CH=CH-CH_2-$;
 27 and the like. The dimer of linoleic acid which is the
 28 preferred embodiment can be expressed in the following
 29 formula:



1 Also the term dimer acid as used herein neces-
2 sarily includes products containing up to about 24 per-
3 cent by weight trimer, but more typically about 10 per-
4 cent by weight trimer since, as is well known in the art,
5 the dimerization reaction provides a product containing
6 a trimer acid having molecular weight of about three times
7 the molecular weight to the starting fatty acid.

8 The polycarboxylic acids or dimer acids noted
9 above are esterified with a glycol, the glycol being an
10 alkane diol or oxa-alkane diol represented by the formula
11 $\text{HO}(\text{RCHCH}_2\text{O})_x\text{H}$ wherein R is H or CH_3 and x is about 2 to
12 100, preferably 2 to 25 with ethylene glycol and diethy-
13 lene glycol particularly preferred. A preferred embodi-
14 ment is formation of the ester with about 1 to 2 moles of
15 glycol per mole of dimer acid or polycarboxylic acid,
16 such as the ester of diethylene glycol with dimerized lin-
17 oleic acid.

18 The oil-soluble alkenyl succinimide ashless dis-
19 persants are those formed by reacting a polyalkenyl suc-
20 cinic acid or anhydride with a polyalkyleneamine. Pre-
21 ferably the alkenyl group is derived from a polymer of a
22 C_2 to C_5 mono-olefin, especially a polyisobutylene where
23 the polyisobutenyl group has a number average molecular
24 weight of about 700 to about 5,000, more preferably about
25 900 to 1,500. The polyamines may be represented by the
26 formula $\text{NH}_2(\text{CH}_2)_n-(\text{NH}(\text{CH}_2)_n)_m-\text{NH}_2$ wherein n is 2 to 3 and
27 m is 0 to 10. Illustrative are ethylene diamine, diethy-
28 lene triamine, triethylene tetramine, tetraethylene pent-
29 amine, which is preferred, pentaethylene hexamine and the
30 like, as well as mixtures of such polyamines. These amines
31 are reacted with the alkenyl succinic acid or anhydride in
32 ratios of about 1:1 to 10:1 moles of alkenyl succinic
33 acid or anhydride to polyamine.

34 The borated alkenyl succinimide dispersants are
35 also well known in the art as disclosed in U.S. Patent
36 3,254,025. These borated derivatives are provided by
37 treating the alkenyl succinimide with a boron compound

1 selected from the class consisting of boron oxides, boron
2 halides, boron acids and esters thereof in an amount to
3 provide from about 0.1 atomic proportion of boron to about
4 10 atomic proportions of boron for each atomic proportion
5 of nitrogen in the dispersant. The borated product will
6 generally contain about 0.1 to 2.0, preferably 0.2 to 0.8
7 weight percent boron based upon the total weight of the
8 borated dispersant. The boron is considered to be present
9 as dehydrated boric acid polymers attaching as the metabor-
10 ate salt of the imide. The boration reaction is readily
11 carried out by adding from about 1 to 3 weight percent,
12 based on the weight of dispersant, of said boron compound,
13 preferably boric acid, to the dispersant as a slurry in
14 mineral oil and heating with stirring as from about 135°C
15 to 165°C for from 1 to 5 hours followed by nitrogen strip-
16 ping and filtration of the product.

17 These alkenyl succinimide ashless dispersants and
18 borated derivatives thereof are used customarily in lubri-
19 cating oil compositions in amounts ranging from 0.1 to 10
20 percent, preferably 0.5 to 5 percent, by weight based upon
21 the total weight of the finished composition.

22 One category of the stabilizer additives of the
23 present invention may generally be defined as the polyol
24 ester of a C_8-C_{22} fatty acid, partial ester meaning at
25 least one hydroxy group remains unreacted. Preferably 1
26 to 3 free OH groups are present such as an average of 1.5
27 to 2.5 free hydroxy groups. Such compounds are, per se,
28 known in the art and it is only their use as a stabilizing
29 agent in a formulated composition containing both the ester
30 friction modifier and alkenyl succinimide dispersant or
31 borated dispersant derivative thereof which is the basis
32 of the present invention.

33 Suitable polyols for preparing the ester stabili-
34 zer of the present invention are those polyhydric alcohols
35 such as glycerol, diglycerol, and the sugar alcohols,
36 which may be represented in the formula $CH_2OH(CHOH)_mCH_2OH$
37 where m is one to five as well as the polyol anhydrides

1 thereof. Preferred are the esters of glycerol itself,
2 $C_3H_5(OH)_3$, sorbitol and sorbitol anhydride (sorbitan).
3 Esters based upon relatively higher, i.e., $C_{12}-C_{22}$, fatty
4 acids or mixtures of fatty acids are more preferable, such
5 as, the tall oil fatty acids. The fatty acids may be satu-
6 rated or unsaturated. Especially preferred are glycerol
7 and sorbitan partial esters of liquid $C_{18}-C_{22}$ unsaturated
8 fatty acids such as oleic, linoleic, and palmitoleic fat-
9 ty acids and mixtures of such acids.

10 Ethoxylated oil-soluble fatty acids, fatty acid
11 amines, and amides have also been found suitable for use
12 as sediment-reducing stabilizer additives in the composi-
13 tions of the present invention. Useful products are those
14 oil-soluble ethoxylated additives of about C_8 to C_{22} satu-
15 rated or unsaturated fatty acids, amines or amides. The
16 degree of ethoxylation of such products is about 2 to 30
17 moles, preferably 1 to 5 moles of ethylene oxide per mole
18 of fatty acid, amine or amide, so that the products retain
19 oil solubility. Derivatives of liquid unsaturated $C_{12}-C_{22}$
20 fatty acids are preferred, such as oleic, linoleic, pal-
21 mitoleic and mixtures thereof, such as the tall oil fatty
22 acids and vegetable oil fatty acids, for example, those
23 derived from cottonseed and soybean oils which contain
24 major amounts of unsaturated C_{18} fatty acids and which are
25 generally liquid at room temperature.

26 Of this category, the oil-soluble ethoxylated
27 fatty acid amines are a preferred embodiment including
28 both fatty acid monoamines and diamines, such as, oil-sol-
29 ule polyethoxylated (1-3 moles of ethylene oxide) coco-
30 amine derived from mixed coconut oil fatty acids ($C_{12}-C_{15}$)
31 and tallow diamine ethoxylates (1-3 moles of ethylene
32 oxide) derived from mixtures of predominantly $C_{16}-C_{18}$ fatty
33 acids.

34 The quantity of sediment-reducing amount of ad-
35 ditive stabilizer of the present invention which is used
36 in a lubricating oil formulation is best expressed rela-
37 tive to the amount of the ester friction-reducing additive

1 which is present. The broad ratio is about 2 to 20 parts
2 by weight of additive stabilizer per part by weight of
3 ester friction-reducing additive with the preferred ratio
4 being about 2 to 12 parts by weight of stabilizer additive
5 per part by weight of friction reducing ester.

6 While the method of addition of the stabilizer
7 additive is largely a function of the exact composition of
8 the total finished formulation, it is generally preferable
9 to provide a blend of stabilizer additive, friction-reduc-
10 ing ester and dispersant by admixing same at moderately
11 elevated temperatures, not greater than 150°F, and incor-
12 porating this blend into the lubricating oil formulation
13 either prior to or subsequent to the addition of other ad-
14 ditives in accordance with blending techniques known in
15 the art.

16 The lubricating oil base stock employed herein
17 are those customarily used: The term lubricating oil in-
18 cludes not only the petroleum hydrocarbon paraffinic,
19 naphthenic, and aromatic oils of lubricating viscosity, but
20 also synthetic oils, such as, polyethylene oils, esters of
21 dicarboxylic acids, complex ester oils, polyglycol, and
22 alcohol alkyl esters of carbonic or phosphoric acids, poly-
23 silicones, fluorohydrocarbon oils and the like. Preferred
24 base stocks are mineral hydrocarbon oils of a paraffinic
25 nature, especially those having a viscosity of about 20 to
26 100 cS min. (100°F) and blends of such mineral paraffinic
27 oils.

28 The stabilizer additives of the present invention
29 are generally effective in substantially eliminating all
30 but traces of sediment when the lubricating oil formulation
31 contains the usually preferred amounts of friction reduc-
32 ing ester component, that is, about 0.05 to 0.3 weight per-
33 cent and therefore, formulations prepared in accordance
34 with the present invention which contain these amounts of
35 friction-reducing ester component are particularly pre-
36 ferred. For formulations containing more than about 0.3
37 weight percent of ester component, there will be in most

1 cases a substantial reduction in the amount of sediment
2 observed after centrifuging as opposed to a complete eli-
3 mination to trace levels.

4 Examples 1-4

5 Lubricating oil formulations were prepared con-
6 taining the dimer acid ester friction modifier and the
7 alkenyl succinimide dispersant to which were added the
8 sediment-reducing additives of the present invention. The
9 formulation was a standard 10W-SAE quality automotive lub-
10 ricating oil composition containing a zinc dialkyl dithio-
11 phosphate, overbased metal sulfonate, rust inhibitor, and
12 VI improver-in typical proportions. At this point the
13 formulation was storage stable with no evidence of sediment
14 formation. To this was added 0.1 percent by weight of a
15 friction modifier being the ester of a dimerized linoleic
16 acid and diethylene glycol and 5 weight percent of the re-
17 action product of 2.1 moles polyisobutenyl ($\bar{M}_n=1300$) suc-
18 cinic anhydride (Sap. No. 103) and 1 mole of alkylene poly-
19 amine to provide the Base Formulation. The polyamine had
20 a composition approximating tetraethylene pentamine and
21 is available under the trade name "DOW E-100" from Dow
22 Chemical Company, Midland, Michigan. Samples (100 ml., cali-
23 brated test tube) of this base formulation were centrifuged
24 for 8, 16 and 24 hours at 1900 r.p.m. at room temperature
25 and thereafter, samples containing the sediment reducing
26 additives of this invention were also tested for compat-
27 ibility by centrifuging under the same conditions. The volume
28 percent sediment was measured on the basis of the sediment observed in
29 a calibrated test tube which contained the 100 ml. samples
30 and the results are set forth in the following Table I.

TABLE I

Vol. % After Centrifuging

| | <u>8 hrs.</u> | <u>16 hrs.</u> | <u>24 hrs.</u> |
|---|---------------|----------------|----------------|
| Base | .20 | .50 | 3.00 |
| Base + Glyceride (Example 1 and 1A) | Trace | Trace | Trace |
| Base + Sorbitan Ester (Example 2) | Trace | Trace | Trace |
| Base + Ethoxylated Cocoamine (Example 3) | - | - | Trace |
| Base + Ethoxylated Tallow Diamine (Example 4) | - | - | Trace |

Example 1: 0.26 weight percent liquid mixture of mono- and diglyceride of oleic acid, 55 percent mono-ester, 130 cps. viscosity at 25°C, sold as ATMOS[®] 300 by ICI America, Inc.

Example 1A: Example 1 was repeated using 0.56 weight percent of the same glyceride with the same results after centrifuging.

Example 2: 1.25 weight percent Sorbitan Mono-oleate liquid having 1900 cps. at 25°C viscosity sold as Arlacel[®] 80 by ICI America, Inc.

Example 3: 1.25 weight percent ethoxylated cocoamine sold as Ethomeen[®] C-12 by ArmaK, Inc., 2 moles ethylene oxide per mole amine, average mol. weight = 285.

Example 4: 1.25 weight percent ethoxylated tallow diamine sold as Ethoduomeen[®] TD-13 by ArmaK, Inc., 3 moles ethylene oxide per mole amine, average mol. weight = 530.

Example 5

A formulation was prepared similar to the base formulation, the preceding Examples except that 0.3 weight percent of the dimer acid ester friction reducing component was used. The base formulation showed about a 3.0 vol. percent sediment formation after 24 hours centrifuging. After addition of 1.25 weight percent of the same gly-

1 ceride of Example 1, the formation was stable after 24
2 hours centrifuging.

3 Example 6

4 Example 5 was repeated with the same results
5 using the same stabilizer additive in the same amount ex-
6 cept that the base formulation contained a borated alkenyl
7 succinimide dispersant prepared by reacting the dispersant
8 of the base formulation with a slurry of 1.4 moles of
9 boric acid in mineral oil over a 3 hour period at 135°
10 to 165°C followed 4 hours of nitrogen stripping. The
11 final product contained 1.5 weight percent nitrogen and
12 0.3 weight percent boron and had a \bar{M}_n of about 3,000.

WHAT WE CLAIM IS:

1. A storage stable lubricating oil composition having a reduced tendency to form sediment comprising a lubricating oil containing

- (a) .01 to 2 percent by weight of a polycarboxylic acid-glycol ester friction reducing component;
- (b) 0.1 to 10 percent by weight of an oil-soluble alkenyl succinimide or borated alkenyl succinimide dispersant; and
- (c) an oil-soluble stabilizer additive being a polyol or polyol anhydride partial ester of a C₈-C₂₂ fatty acid, an ethoxylated C₈-C₂₂ fatty acid, fatty amine or fatty amide, in an amount effective to reduce the tendency of said lubricating oil compositions to form sediment.

2. The composition of claim 1 wherein said (a) component is a dimer acid ester of an unsaturated fatty acid having from about 16 to 22 carbon atoms between the carboxylic acid groups of said dimer acid.

3. The composition of claims 1 or 2 wherein there is present 0.05 to 0.5 percent by weight of said (a) component based on the total weight of the lubricating oil composition.

4. The composition of claims 1-3, wherein said (c) component is a glycerol partial mono- or di-ester of oleic, linoleic or palmitoleic acid or a mixture of said acids.

5. The composition of claim 4 wherein said (c) component is a mixture of glycerol mono- and di-esters of oleic acid.

6. The composition of claim 3 wherein said (c) component is a sorbitan partial ester of oleic acid.

7. The composition of claim 3 wherein said (c) component is an ethoxylated C₁₂-C₁₈ fatty monoamine or diamine containing 1 to 3 mole of ethylene oxide per mole of said monoamine or diamine.

8. The composition of claims 1-7 wherein the weight ratio in parts by weight of said (c) component to said (a) component is from 2 to 20 parts by weight of said (c) component per part by weight of said (a) component.

9. The composition of claims 1-8 wherein said (a) component is diethylene glycol ester of dimerized linoleic acid present in an amount from about 0.1 to 0.3 weight percent, based on the total weight of the composition.

10. The composition of claims 1-9 wherein said (b) dispersant component is a polyisobutenyl succinic anhydride-polyalkyleneamine reaction product or borated polyisobutenyl succinimide.



European Patent
Office

EUROPEAN SEARCH REPORT

0039998

Application number

EP 81 30 1562

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | CLASSIFICATION OF THE APPLICATION (Int. Cl.) |
|--|--|--|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | |
| DX | US - A - 4 105 571 (H. SHAUB) * Claims 1,2,5-11; column 3, line 66 - column 5, line 50; column 6, lines 56-65; column 11, lines 9-16; column 12, lines 5-6 * & NL - A - 78 07606 & FR - A - 2 401 218 -- | 1-4,6, 8-10 | C 10 M 1/14 3/08 |
| D | US - A - 3 933 659 (R.E. LYLE) * Claims 1-8 * & FR - A - 2 277 882 -- | 1,7,10 | TECHNICAL FIELDS SEARCHED (Int. Cl.) C 10 M 1/14 3/08 |
| D | US - A - 3 172 892 (W.M. LESUER) * Claims 1-6 * -- | 10 | |
| D | US - A - 3 254 025 (W.M. LESUER) * Claims 1-12 * ---- | 10 | |
| | | | CATEGORY OF CITED DOCUMENTS |
| | | | X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons |
| | | | &: member of the same patent family, corresponding document |
| + The present search report has been drawn up for all claims | | | |
| Place of search The Hague | | Date of completion of the search 21-08-1981 | Examiner RO TSAERT |

EPO Form 1503.1 08.78

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